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(54) Resin modifier and modified resin.

(57) A polymer such as polyester is modified by reaction with a compound having the formula:

$$Y_1 - \underset{\displaystyle (X)_n}{\underset{|}{Z}} - Y_2$$

in which X is halogen, each of Y1 and Y2 is a three-to eight-membered ring, Z is a divalent organic group and n is an integer.

EP 0 314 303 A2

RESIN MODIFIER AND MODIFIED RESIN

The present invention relates to a resin modifier capable of imparting fire retardance to a resin through a simple method and a resin modified by making use of the same and more particularly to a resin modifier capable of not only imparting thermal stability and flexibility to a resin but also giving a surface appearance free from bleeding thereof from the resin and a resin modified therewith.

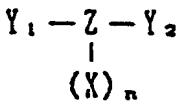
[Prior Art]

Various methods are known with respect to the impartation of fire retardance to a resin. These methods are classified broadly into an addition type method and a reaction type method. In the former method, antimony hydroxide, antimony trioxide, boron compounds, bromine compounds, and phosphorus compounds are used, and flame retardation can be attained through a simple method. However, the former method is disadvantageous in that the compound is bled from the surface of the resin in a prolonged exposure or a heating atmosphere to spoil the surface appearance and lower the flexibility. In the latter method, an epoxy group, a vinyl group, an ester forming functional group, or the like is introduced as a reactive group into a monomer, an oligomer, and a polymer of a bromine compound, a phosphorus compound, or the like, and these fire-retardant groups are incorporated into the molecular skeleton or incorporated into a polymer molecule through a reaction between polymers. The reaction type method not only is free from bleeding but also can impart flexibility and therefore is a useful method which can eliminate the drawbacks of the former method. However, in the latter method, complicated procedures are required in order to incorporate a fire-retardant monomer into a polymer skeleton because no increase in the degree of polymerization can be attained by an ordinary method. The addition of a reactive fire-retardant oligomer or polymer is a simple expedient to overcome such a difficulty. However, this method unfavorably brings about an interaction between the additive and the base polymer during kneading, which leads to lowering in both the molecular weight and the mechanical properties. This tendency is remarkable in polyesters and polyamides.

(Summary of the Invention)

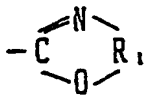
In view of the above-described problems, the present inventors have made extensive and intensive studies with a view to developing a simple method which can impart to a polymer thermal stability, flexibility and other physical properties and an excellent surface appearance without causing a lowering in the mechanical properties while imparting fire retardance thereto and, as a result, have found that a particular compound has an excellent effect, which has led to the completion of the present invention.

Specifically, the present invention provides a resin modifier comprising a compound represented by the following general formula (1):

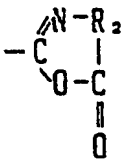


(1)

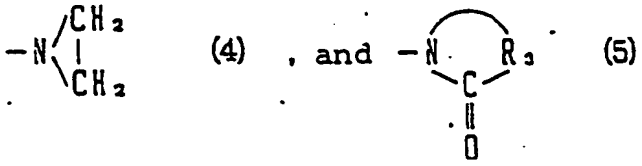
wherein X is a halogen, Y_1 and Y_2, which may be the same or different, are each a three- to eight-membered cyclic reactive group selected from among functional groups represented by the following general formulae (2) to (5):



(2) ,



(3) ,



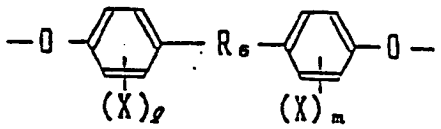
(4) , and (5)

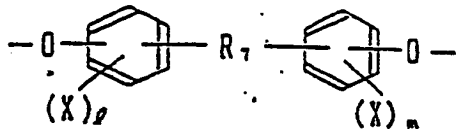
wherein R_1 to R_3 are each a divalent organic group, provided that hydrogen directly attached to the ring may be substituted with an alkyl and/or an aryl, Z is a divalent organic group and n is an integer of 1 or more, and a resin modified with said modifier.

It is preferred in the formulae (1) to (5) that R1 to R3 each are a straight alkylene having 1 to 6 carbon atoms and may have a substituent(s) such as an alkyl having 1 to 10 carbon atoms, more preferably 1 to 6, and an aryl having 6 to 12 carbon atoms, more preferably phenyl, provided that the groups (2), (3) and (5) each is a 3- to 8-membered ring. It is more preferable that R1 is ethylene or ethylene group having a C1 to C6 alkyl or phenyl; R2 is methylene or ethylene which may have a substituent(s) such as a C1 to C4 alkyl or phenyl; R3 is a straight C3 to C5 alkylene which may have a substituent(s) such as a C1 to C4 alkyl or phenyl. It is preferable that -Z(X)n- is selected from the groups (6) to (12). It may contain two or more groups selected from the groups (6) to (12). When a dicarboxylic compound and a bisoxazoline such as 2,2´-m-phenylene-bis(2-oxazolin) are reacted with each other, two groups are contained in Z.

In the general formula (1), X is a halogen, and examples thereof include chlorine and bromine. Bromine is more preferable from the viewpoint of prevention of environmental pollution.

It is preferred that the group represented by the formula $-Z-_{(X)n}$ in the formula (1) representing the compound constituting the modifier of the present invention be a divalent organic group containing at least one residue of a brominated diol, a brominated carboxylic acid, a brominated diglycidyl ester and/or a brominated diglycidyl ether, etc. each having a molecular weight of 390 or more. Particularly preferable examples of the residue include those of a brominated diol and/or a brominated dicarboxylic acid. Specific examples of the organic group include a divalent organic group having, as the constituent unit, at least one of at least one kind of groups represented by the following general formulae (6) to (12):


(6),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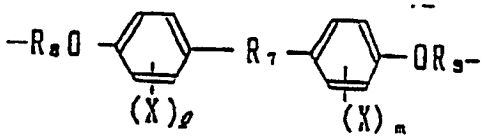
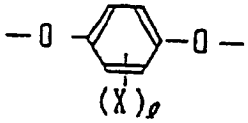
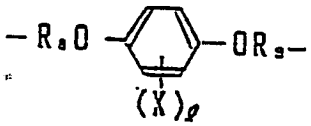
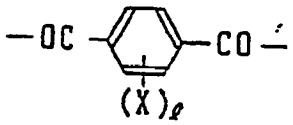
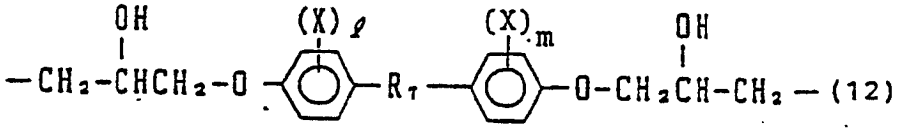

(8),

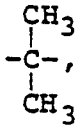

(9),


(10),


(11), and


(12)

wherein R_6 and R_7 are each $-CH_2-$,



$-O-$, $-S-$, or $-SO_2-$;

R_8 and R_9 are each $-C_2H_4-$, $-C_3H_6-$, $-(C_2H_4O)n-$, or $-(C_3H_6O)n-$;

ℓ and m are each an integer of 1 to 4; and X and n are as defined above.

When bromine is used as the halogen, examples of the group represented by the general formula (6) include residues of tetrabromobisphenol A and tetrabromobisphenol sulfone, examples of the group represented by the general formula (7) include a residue of tetrabromobisphenol F, examples of the group

represented by the general formula (8) include residues of an adduct of tetrabromobisphenol A with 2 mol of ethylene oxide, an adduct of tetrabromobisphenol A with 2 mol of propylene oxide, an adduct of tetrabromobisphenol sulfone with 2 mol of ethylene oxide, and an adduct of tetrabromobisphenol sulfone with 2 mol of propylene oxide, examples of the group represented by the general formula (9) include a residue of tetrabromohydroquinone, examples of the group represented by the general formula (10) include a residue of an adduct of tetrabromohydroquinone with 2 mol of ethylene oxide, and examples of the group represented by the general formula (11) include a residue of tetrabromoterephthalic acid.

These bromine compounds may be used alone. Further, they may also be used in the form of a divalent organic group incorporated as a repeating unit into an oligomer or a polymer prepared by reacting these bromine compounds with other compounds, such as dicarboxylic acid, diol, or diepoxide.

The three- to eight-membered cyclic reactive groups represented by the above general formulae (2) to (5) may be introduced by various methods.

The group represented by the above formula (2) is preferably a group wherein R_1 is an ethylene group, i.e., oxazoline. The oxazoline may be produced by an expedient such as a reaction of a carboxylic acid with ethanolamine. Alternatively, an oxazoline compound which has previously been prepared may be subjected to an addition reaction to prepare the compound represented by the above formula (1). Particularly, in the latter case, it is preferable from the viewpoint of the reactivity to use a bisoxazoline compound. If desired, it is possible to use a catalyst such as a tertiary amine or a phosphine in the reaction of the oxazoline.

Specific examples of the bisoxazoline compound for introducing the group represented by the above formula (2) include 2,2′-methylenebis(2-oxazoline), 2,2′-ethylenebis(2-oxazoline), 2-2′-ethylenebis(4-methyl-2-oxazoline), 2,2′-propylenebis(2-oxazoline), 2,2′-tetramethylenebis(2-oxazoline), 2,2′-hexamethylenebis(2-oxazoline), 2,2′-octamethylenebis(2-oxazoline), 2,2′-p-phenylenebis(2-oxazoline), 2,2′-p-phenylenebis(4-methyl-2-oxazoline), 2,2′-p-phenylenebis(4,4-dimethyl-2-oxazoline), 2,2′-p-phenylenebis(4-phenyl-2-oxazoline), 2,2′-m-phenylenebis(2-oxazoline), 2,2′-m-phenylenebis(4-methyl-2-oxazoline),2,2′-m-phenylenebis-(4,4-dimethyl-2-oxazoline), 2,2′-m-phenylenebis(4-phenyl-2-oxazoline), 2,2′-o-phenylenebis(2-oxazoline), 2,2′-phenylbis(4-methyl-2-oxazoline), 2,2′-bis(2-oxazoline), 2,2′-bis(4-methyl-2-oxazoline), 2,2′-bis(4-ethyl-2-oxazoline), and 2,2′-bis(4-phenyl-2-oxazoline). These bisoxazoline compounds may be used alone or in a combination of two or more of them.

Among these bisoxazoline compounds, those containing an aromatic ring group are preferable, and those containing a phenylene group are more preferable. A particularly preferable bisoxazoline compound is 2,2′-m-phenylenebis(2-oxazoline).

The group represented by the above general formula (3) is preferably a group wherein R_2 is methylene, i.e., oxazolone, and a group wherein R_2 is ethylene, i.e., oxazinone. These groups can easily be prepared by dehydrating an N-acyl-α-amino carboxylic acid or an N-acyl-β-amino carboxylic acid with, e.g., acetic anhydride. Therefore, these groups may be introduced as a terminal of a derivative of a compound represented by the above formula (1) by the above-described method. Alternatively, bisoxazolone or bisoxazinone which has previously been prepared may be bonded to the terminal through a reaction to prepare a compound represented by the above formula (1).

Examples of the bisoxazolone compound include 2,2′-bis(5(4H)-oxazolone), 2,2′-methylenebis(5(4H)-oxazolone), 2,2′-ethylenebis(5(4H)-oxazolone), 2,2′-tetramethylenebis(5(4H-oxazolone), 2,2′-hexamethylenebis(5(4H)-oxazolone), 2,2′-decamethylenebis(5(4H)-oxazolone), 2,2′-p-phenylenebis(5(4H)-oxazolone), 2,2′-m-phenylenebis(5(4H)-oxazolone), 2,2′-naphthalenebis(5(4H)-oxazolone), 2,2′-diphenylenebis-(5(4H)-oxazolone), 2,2′-(1,4-cyclohexylene)-bis(5(4H)-oxazolone), 2,2′-bis(4-methyl-5(4H)-oxazolone), 2,2′-methylenebis(4-methyl-5(4H)-oxazolone), 2,2′-ethylenebis(4-methyl-5(4H)-oxazolone), 2,2′-tetramethylenebis(4-methyl-5(4H)-oxazolone), 2,2′-hexamethylenebis(4-methyl-5(4H)-oxazolone), 2,2′-decamethylenebis(4-methyl-5(4H)-oxazolone), 2,2′-p-phenylenebis(4-methyl-5(4H)-oxazolone), 2,2′-m-phenylenebis(4-methyl-5(4H)-oxazolone), 2,2′-naphthalenebis(4-methyl-5(4H)-oxazolone), 2,2′-diphenylenebis(4-methyl-5(4H)-oxazolone), 2,2′-(1,4-cyclohexylene)-bis(4-methyl-5(4H)-oxazolone), 2,2′-bis-(4,4-dimethyl-5(4H)-oxazolone), 2,2′-methylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-ethylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-tetramethylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-hexamethylenebis-(4,4-dimethyl-5(4H)-oxazolone), 2,2′-octamethylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-decamethylenebis(4,4- dimethyl-5(4H)-oxazolone), 2,2′-p-phenylenebis(4,4-dimethyl)-5(4H)-oxazolone), 2,2′-m-phenylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-naphthalenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-diphenylenebis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-(1,4-cyclohexylene)-bis(4,4-dimethyl-5(4H)-oxazolone), 2,2′-bis(4-isopropyl-5(4H)-oxazolone), 2,2′-methylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-ethylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-tetramethylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-hexamethylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-p-phenylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-m-phenylenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-naphthalenebis(4-isopropyl-5(4H)-oxazolone), 2,2′-bis(4-isobutyl-5(4H)-ox-

azolone), 2,2′-methylenebis(4-isobutyl-5(4H)-oxazolone), 2,2′-ethylenebis(4-isobutyl-5(4H)-oxazolone), 2,2′-tetramethylenebis(4-isobutyl-5(4H)-oxazolone), 2,2′-hexamethylenebis(4-isobutyl-5(4H)-oxazolone), 2,2′-p-phenylenebis(4-isobutyl-5(4H)-oxazolone), 2,2′-m-phenylenebis(4-isobutyl-5(4H)-oxazolone), and 2,2′-naphthalenebis(4-isobutyl-5(4H)-oxazolone).

Examples of the bisoxazinone compound include 2,2′-bis(3,1-benzoxazin-4-one), 2,2′-methylenebis(3,1-benzoxazin-4-one), 2,2′-ethylenebis(3,1-benzoxazin- 4-one), 2,2′-tetramethylenebis(3,1-benzoxazin-4-one), 2,2′-hexamethylenebis(3,1-benzoxazin-4-one), 2,2′-decamethylenebis(3,1-benzoxazin-4-one), 2,2′-p-phenylenebis(3,1-benzoxazin-4-one), 2,2-m-phenylenebis(3,1-benzoxazin-4-one), 2,2′-naphthalenebis(3,1-benzoxazin-4-one), 2,2′-(4,4-diphenylene)bis(3,1-benzoxazin-4-one), 2,2′-(1,4-cyclohexylene)bis(3,1-benzoxazin-4-one), 2,2′-bis(4,4-dihydro-1,3,6H-oxazin-6-one), 2,2′-methylenebis(4,5-dihydro-1,3,6H-oxazin-6-one), 2,2′-ethylenebis(4,5-dihydro-1,3,6H-oxazin-6-one), 2,2′-tetramethylenebis(4,5-dihydro-1,3,6H-oxazin-6-one), 2,2′-p-phenylenebis(4,5-dihydro-1,3,6H-oxazin-6-one), 2,2′-m-phenylenebis(4,5-dihydro-1,3,6H-oxazin-6-one), 2,2′-bis(4-methyl-5-hydro-1,3,6H-oxazin-6-one), 2,2′-ethylenebis(4-methyl-5-hydro-1,3,6H-oxazin-6-one), 2,2′-o-phenylenebis(4-methyl-5-hydro-1,3,6H-oxazin-6-one), 2,2′-m-phenylene(4-methyl-5-hydro-1,3,6H-oxazin-6-one), 2,2′-p-phenylenebis(4-hydro-5-methyl-1,3,6H-oxazin-6-one), and 2,2′m-phenylenebis-(4-hydro-5-methyl-1,3,6H-oxazin-6-one).

The aziridine group represented by the above formula (4) can easily be produced by reacting ethyleneimine with an acid chloride or an isocyanate compound. It is preferred to bond a bisaziridine compound prepared by reacting ethyleneimine with a diisocyanate compound to the terminal of a compound having the above-described group represented by the formula $-\underset{\underset{(X)_n}{|}}{Z}-$ through a reaction to prepare a compound represented by the above formula (1).

The lactam group represented by the above formula (5) is preferably a group wherein R_3 is trimethylene, i.e., pyrrolidone, a group wherein R_3 is tetramethylene, i.e., piperidone, and a group wherein R_3 is pentamethylene, i.e., caprolactam. As with the group represented by the above formula (4), the lactam group represented by the above formula (5) can easily be prepared by reacting a lactam with an acid chloride or an isocyanate compound.

The functional groups respectively represented by the formulae (4) and (5) may be introduced by treating the terminal of the above-described compound having a group represented by the formula $-\underset{\underset{(X)_n}{|}}{Z}-$ with these substances. Alternatively, these groups may be introduced into the terminal of the group represented by the formula $-\underset{\underset{(X)_n}{|}}{Z}-$ in the form of bisaziridine or bislactam which has previously been reacted with a diisocyanate compound. Examples of the acid chloride used in these reactions include derivatives of terephthalic, isophthalic, naphthalenedicarboxylic, adipic, sebacic, trimellitic and succinic acids.

Examples of the diisocyanate include toluene diisocyanate, methylenediphenyl diisocyanate, xylylene diisocyanate, naphthylene diisocyanate, 3,3′-dimethyldiphenyl 4,4′-diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, a hydrogenation product of methylenebiphenyl diisocyanate, a hydrogenation production of toluene diisocyanate, lysine diisocyanate, and bis(2-isocyanatoethyl) fumarate.

The molecular weight of the compound represented by the formula (1) is preferably 500 to 5,000. When the molecular weight is less than 500, the efficiency of the impartation of fire retardance is poor. On the other hand, when the molecular weight exceeds 5,000, the mechanical properties of the added polymer are unfavorably spoiled.

Representative examples of a substance which may be modified by addition of a modifier comprising a compound represented by the formula (1) according to the present invention include a polymer having in its chain at least one group of at least one member selected from among carboxylate, hydroxyl, amino, amide, and epoxy groups, etc. These groups may be bonded to not only the terminal of the polymer chain but also the polymer chain in a pendant form.

Examples of these polymers include polyester, polyamide, polyamic acid, polyimide, polyester amide, and polyepoxide. They may be used alone or in any combination of two or more of them.

The modifier of the present invention is used in an amount of preferably 0.1 to 70% by weight based on the polymer to be modified. The modifier of the present invention may simply be added to and kneaded with a polymer to be modified by an ordinary method, thereby attaining a modification effect on the fire retardance or the like. Further, it is also possible to react part or the whole of the modifier with the polymer so that the modifier serves as a component of the polymer. Specifically, the modifier compound represented by the formula (1) may be reacted with at least one compound having at least two of at least one

functional group selected from among carboxylate, hydroxyl, amino, amide, and epoxy groups to prepare a polymer. The polymer thus obtained is remarkably excellent in fire retardance.

The modified resin of the present invention can easily be prepared by kneading, in a molten state, the modifier of the present invention with the resin to be modified as described above by making use of a single-screw or multi-screw extruder according to an ordinary method, followed by molding. Particularly, when the formation of a chemical bond through a reaction of a modifier with a resin is intended, a combined use of a suitable reaction accelerator is more effective.

Further, the modified resin of the present invention may be used in the form of a composition containing a modified resin according to the purposes by adding and kneading conventional additives generally known as an additive for a resin composition with the modified resin of the present invention during the preparation thereof or in a separate manner. Examples of the additive and filler useful for this purpose include at least one member selected from among plasticizers, stabilizers such as antioxidants and ultraviolet absorbers, antistatic agents, surface treatments, surfactants, flameproof auxiliaries, colorants such as dyes and pigments, lubricants for improving flowability and releasability, lubricating agents, crystallization accelerators (nucleating agents), inorganic or high-melting organic fibrous reinforcements such as glass fiber and carbon fiber, or particulate or sheet-form inorganic fillers.

As is apparent from the description and the examples, the present invention provides a novel resin modifier, and a modified resin prepared by making use of the resin modifier of the present invention is a resin which has sufficient fire retardance and further, as opposed to the resin fire-retarded by the conventional method, causes no lowering in mechanical properties, has excellent heat resistance, and causes neither deterioration of the surface appearance nor other unfavorable phenomena due to the bleeding of the fire retardant or the like, i.e., has a combination of excellent fire retardance with other various excellent properties.

[Examples]

The present invention will now be described with reference to the following Examples which should not be construed as limiting the scope of the present invention.

Referential Example 1

<Preparation of a compound represented by the general formula (1)>

54.4 parts by weight of tetrabromobisphenol A, 45.2 parts by weight of m-phenylenebisoxazoline, and 0.5 part by weight of triphenylphosphine were heated under reflux for 4 hr in a xylene-acetone mixed solvent. The reaction mixture was washed with methanol and chloroform to prepare 64.3 parts by weight of a reaction product. It was confirmed by FT-IR and NMR analyses that the reaction product was a compound having an oxazoline ring at its both terminals. The compound thus prepared will be abbreviated to "TBA-BoZ". A product of a reaction of tetrabromobisphenol A with 2,2-bis(5(4H)-oxazolone) (abbreviated to "TBA-BoZN"), a product of a reaction of a tetrabromobisphenol sulfone/ethylene oxide (2 mol) adduct with 2,2′-bis(5(4H)-oxazolone) (abbreviated to "TBS-2EO-BoZN"), a product of a reaction of tetrabromoterephthalic acid with diphenylmethane-bis-(4,4′-N,N′-diethyleneurea) (abbreviated to "TBTA-MDI-EI"), and a product of a reaction of tetrabromobisphenol A with diphenylmethanebis(4,4′-carbamoyl-ε-caprolactam) (abbreviated to "TBA-MDI-CPL") were prepared in the same manner as that described above.

Further, 51.0 parts by weight of dimethyl tetrabromoterephthalate, 19.2 parts by weight of dimethyl isophthalate, and 126.4 parts by weight of an adduct of tetrabromobisphenol A with 2 mol of ethylene oxide were melted in a reactor and reacted under reduced pressure, thereby preparing an oligomer having a yellowish brown color. The oligomer thus prepared was subjected to gel permeation chromatography and found to have an average molecular weight of 3,200. To 100 parts by weight of the above-prepared oligomer was added 13.5 parts by weight of m-phenylenebisoxazoline. The mixture was allowed to react for 30 min while melting at 260° C in a nitrogen gas stream. The reaction mixture was allowed to cool and ground to prepare an oligomer powder (abbreviated to "BrEST-BoZ").

Example 1

87.5 parts by weight of polybutylene terephthalate (PBT) was mixed with 12.5 parts by weight of the powdery modifier compound TBA-BoZ as prepared above, followed by homogeneous melt mixing with an ordinary extruder to form pellets. Specimens were prepared from the pellets by making use of an injection molding machine according to an ordinary method to evaluate the physical properties.

The physical properties were measured by the following methods.

The tensile strength and degree of elongation (%) were measured according to ASTM D 638, while the Izod impact strength was measured according to ASTM D 256. The breakdown strength was measured by the short-term test according to ASTM D 149. With respect to the surface appearance, the specimen was maintained at 120°C for 72 hr to observe the surface. When abnormal phenomena, such as bleeding or blistering, were observed on the surface, the surface appearance was regarded as poor (X), while when the surface was free from such abnormal phenomena, the surface appearance was regarded as good (O). The oxygen index was measured according to JIS K 7201.

A tensile specimen was stored in a thermostatted bath of 120°C for 500 hr and then subjected to measurement of the degree of elongation in the same manner as that described above, followed by calculation of percentage retention of elongation. Further, a sheet having a thickness of 200 μm was prepared by means of a hot press. After the sheet was stored at 120°C for 500 hr, it was folded ten times at an angle of 90°. Thereafter, the surface appearance was examined to evaluate the flexibility. When abnormal phenomena, such as occurrence of breaking and fine cracks, were observed on the surface, the flexibility was regarded as poor (X), while when the surface was free from such abnormal phenomena, the flexibility was regarded as good (O). The results of each measurement are shown in Table 1.

Examples 2 to 6

Specimens were prepared by making use of various modifiers prepared above according to the formulation shown in Table 1 in the same manner as that of Example 1. The physical properties of the specimens were measured, and the results are shown in Table 1.

Comparative Example 1

The same procedures as those of Example 1 were repeated, except that 12.5 parts by weight of decabromodiphenyl ether was used as the fire retardant. The results are shown in Table 1.

Table 1

		PBT						
		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Comp. Ex. 1
additives	TBA-BoZ (pts. by wt.)	12.5	--	--	--	--	--	--
	TBA-BoZN (pts. by wt.)	--	12.5	--	--	--	--	--
	TBS-2EO-BoZN (pts. by wt.)	--	--	12.5	--	--	--	--
	TBTA-MDI-EI (pts. by wt.)	--	--	--	12.5	--	--	--
	TBA-MDI-CPL (pts. by wt.)	--	--	--	--	12.5	--	--
	BrEST-Boz (pts. by wt.)	--	--	--	--	--	12.5	--
	fire retardant (pts. by wt.)	--	--	--	--	--	--	12.5
tensile strength (kg/cm^2)		585	580	582	579	564	575	540
percentage elongation in tension (%)		354	351	355	342	310	356	70
Izod impact strength (notched) (kg-cm/cm)		14	14	16	14	11	7.0	2.6
breakdown strength		16	16	16	16	16	16	14
surface appearance		O	O	O	O	O	O	X
oxygen index		27	27	27	27	27	27	27
after heat treatment for 500 hr	tensile strength	297	288	309	274	245	310	12
	percentage retention of elongation (%)	84	82	87	80	79	87	17
	flexibility	O	O	O	O	O	O	X

Examples 7 to 9

The modifiers as shown in Table 2 were mixed with a polymer in the same manner as that of Example 1, except that an aromatic polyester (PAR) comprising terephthalic acid, isophthalic acid, and bisphenol A was used as the resin to be modified, thereby preparing specimens, followed by measurements of the physical properties of the specimens. The results are shown in Table 2.

Comparative Example 2

Decabromodiphenyl ether was used instead of the modifiers used in Examples 7 to 9. The results are shown in Table 2.

Examples 10 to 12

Specimens were prepared in the same manner as that of Example 1, except that nylon 66 comprising adipic acid and hexamethylenediamine was used as the resin to be modified, to evaluate the physical properties. The results are shown in Table 2.

Comparative Example 3

The results in the case where decabromodiphenyl ether was used instead of the modifiers used in

Examples 10 to 12 are also shown in Table 2.

Table 2

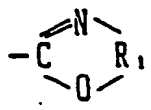
		PAR				nylon 66			
		Ex. 7	Ex. 8	Ex. 9	Comp. Ex. 2	Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 3
additive	TBA-BoZ (pts. by wt.)	4	--	--	--	6	--	--	--
	TBTA-MDI-EI (pts. by wt.)	--	4	--	--	--	6	--	--
	BrEST-BoZ (pts. by wt.)	--	--	4	--	--	--	6	--
	fire retardant (pts. by wt.)	--	--	--	4	--	--	--	6
tensile strength (kg/cm^2)		740	730	730	710	870	865	850	835
percentage elongation in tension (%)		110	120	140	50	89	87	95	48
Izod impact strength (notched) (kg-cm/cm)		20	20	24	15	9.0	8.5	11	3.9
breakdown strength		24	24	24	20	24	24	24	21
surface appearance		O	O	O	X	O	O	O	X
oxygen index		29	29	29	29	28	28	28	28
after heat treatment for 500 hr	tensile strength	76	78	94	23	54	48	51	4
	percentage retention of elongation (%)	69	65	67	45	61	55	54	19
	flexibility	O	O	O	X	O	O	O	X

Claims

1. A resin modifier comprising a compound represented by the following general formula (1):

$$Y_1 - Z(X)_n - Y_2 \qquad (1)$$

wherein X is a halogen, Y_1 and Y_2, which may be the same or different, are each a three- to eight-membered cyclic reactive group selected from among functional groups represented by the following general formulae (2) to (5):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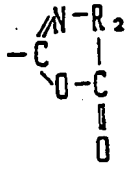
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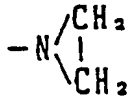
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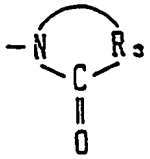

(5)

wherein R_1 to R_3 are each a divalent organic group, provided that hydrogen directly attached to the ring may be substituted with an alkyl and/or an aryl, Z is a divalent organic group and n is an integer of 1 or more.

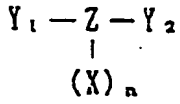
2. A resin modifier according to claim 1, wherein the group represented by the formula $-\underset{(X)n}{\overset{|}{Z}}-$ in the general formula (1) is a group containing at least one residue of a halogenated diol and/or a halogenated dicarboxylic acid having a molecular weight of 390 or more.

3. A resin modifier according to claim 1 or 2, wherein said halogen (X) is bromine.

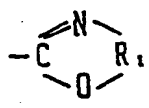
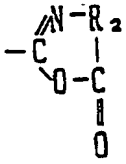
4. A resin modifier according to any one of claims 1 to 3, wherein said compound represented by the general formula (1) is a compound prepared by reacting a compound having at least two reactive groups selected from among the groups represented by the general formulae (2) to (5) with a halogenated diol and/or a halogenated dicarboxylic acid having a molecular weight of 390 or more or a derivative thereof.

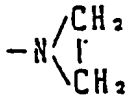
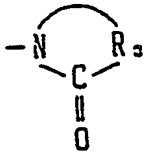
5. A resin modifier according to any one of claims 1 to 4, wherein said compound represented by the general formula (1) has a molecular weight of 500 to 5,000.

6. A modified resin produced by reacting a polymer having at least two of at least one functional group selected from the group consisting of carboxylate, hydroxyl, amino, amide, and epoxy groups with a compound represented by the following general formula (1):


(1)

wherein X is a halogen, Y_1 and Y_2, which may be the same or different, are each a three- to eight-membered cyclic reactive group selected from among functional groups represented by the following general formulae (2) to (5):


(2)

(3),


(4), and

(5)

wherein R_1 to R_3 are each a divalent organic group, provided that hydrogen directly attached to the ring may be substituted with an alkyl and/or an aryl, Z is a divalent organic group and n is an integer of 1 or

more.

7. A modified resin according to claim 6, in which the compound is reacted with the polymer in an amount of 0.1 to 70 wt.%, based on the polymer.

8. A modified resin according to claim 6, in which the polymer is selected from the group consisting of polyesters, polyamides, polyamic acids, polyimides, polyester amides and polyepoxides.

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(54) Resin modifier and modified resin.

(57) A polymer such as polyester is modified by reaction with a compound having the formula:

$$Y_1 - Z - Y_2$$
$$|$$
$$(X)_n$$

in which X is halogen, each of Y1 and Y2 is a three- to eight-membered ring, Z is a divalent organic group and n is an integer.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 8951

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	EP-A-0 273 368 (TEIJIN) * Examples 12-15,21,30-38,44,46; claims 37-40 * ---	1-8	C 08 G 85/00 C 08 G 63/68
A	EP-A-0 019 061 (TEIJIN) ---		
A	JOURNAL OF APPLIED POLYMER SCIENCE, vol. 30, no. 8, August 1985, pages 3325-3337, John Wiley & Sons, Inc., New York, US; H. INATA et al.: "Chain extenders for polyesters. I. Addition-type chain extenders reactive with carboxyl end groups of polyesters" ---		
A	EP-A-0 141 345 (TAKEDA CHEMICAL IND.) ---		
P,A	JOURNAL OF APPLIED POLYMER SCIENCE, vol. 34, no. 8, december 1987, pages 2769-2776, John Wiley & Sons, Inc., New York, US; H. INATA et al.: "Chain extenders for polyesters. VI. Properties of the polyesters chain-extended by 2,2'-Bis(4H-3,1-benzoxazin-4-one)" ---		TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 08 G
A	JOURNAL OF APPLIED POLYMER SCIENCE, vol. 32, no. 4, September 1986, pages 4581-4594, John Wiley & Sons, Inc, New York, US; H. INATA et al.: "Chain extenders for polyesters. III. Addition-type nitrogen-containing chain extenders reactive with hydroxyl end groups of polyesters" --- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-08-1990	KLIER E.K.

CATEGORY OF CITED DOCUMENTS

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 233 (C-304)[1956], 19th September 1985; & JP-A-60 90 219 (TAKEDA YAKUHIN KOGYO K.K.) 21-05-1985 * Whole document *	1-8	
E	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 158 (C-586)[3506], 17th April 1989; & JP-A-63 314 243 (TEIJIN LTD) 22-12-1988 * Whole document *	1-5	
E	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 63 (C-568)[3411], 13th February 1989; & JP-A-63 256 645 (POLYPLASTICS CO.) 24-10-1988 * Whole document *	1-8	
X	WPIL, FILE SUPPLIER, accession no. 87-254834, Derwent Publications Ltd, London, GB; & JP-A-62 177 212 (UNITIKA K.K.) 04-08-1987 * Whole abstract *	1,5-8	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	WPIL, FILE SUPPLIER, accession no. 87-254835, Derwent Publications Ltd, London, GB; & JP-A-62 177 213 (UNITIKA K.K.) 04-08-1987 * Whole abstract *	1,5-8	

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